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# Anomalous Green Luminescent Properties in CVD Synthetic Diamonds

Amber M. Wassell, Colin D. McGuinness, Chris Hodges, Peter M. P. Lanigan, David Fisher, Philip M. Martineau, Mark E. Newton, and Stephen A. Lynch\*

In this paper, the authors explore the spectral properties of a sharp emission line centered at 499.6 nm (reported previously as 499 nm) observed in the UV-luminescence spectrum of synthetic CVD diamond gemstones. These gemstones also exhibit spectrally prompt broad blue luminescence centered at 435 nm which is similar in character to the 425 nm blue luminescence characteristic of type IIa natural diamonds. By comparing the results against synthetic CVD diamond material which has been subjected to high temperature anneals, the authors can speculate on the nature of the defect associated with this color center. Since the 499 nm spectral line has only been observed in synthetic CVD diamonds to date, the authors further propose that it can be helpful in the identification of synthetic diamonds, in particular those showing the blue luminescence signature usually associated with type IIa natural diamonds.

## 1. Introduction


The unique combination of diamond's optical and mechanical properties mean that it is prized above all other materials as a gemstone. When these properties are considered alongside the rarity of natural diamond, the intrinsic value attached to natural diamond material is significant. In 2017, the estimated global diamond production was around 140 million carats with a value of over \$15 billion.<sup>[1]</sup> A key aspect of maintaining this high

market value is consumer confidence. Synthetic gemstone quality diamond material can now be produced by high pressure high temperature (HPHT), or by chemical vapor deposition (CVD) growth methods. However, since natural untreated diamonds are valued above treated diamonds or synthetics, customers need to be convinced that undisclosed synthetics can be detected with a high degree of confidence. Numerous interrogation methods are currently employed by gemmologists to verify the origin of a gemstone. One of the most powerful analytical weapons in the gemmologist's armory is optical spectroscopy because it can record the optical characteristics of a gemstone in a way that is quantifiable and reproducible. Certain optical signatures

will raise concerns because they indicate the presence of additional elements, or point and extended defects, not commonly found in natural diamonds. Likewise, certain optical signatures can also reveal clues about the growth conditions when the crystal was forming, conditions that will be significantly different for natural and synthetic diamonds. The vast majority of natural type IIa diamonds are known to exhibit blue fluorescence (centered at 425 nm) attributed to the occurrence of dislocations, when excited by short wave UV radiation ( $\lambda < 225$  nm).<sup>[2]</sup> This emission shows a characteristic polygonized network pattern and is one of the underlying principles behind the use of the De Beers DiamondView instrument (marketed and distributed by IIDGR) in identifying natural diamonds. Recently, we have observed a blue fluorescence signature in diamond gemstones known to be of a synthetic CVD origin. Techniques have been developed to continue to use DiamondView to identify such synthetic diamonds.<sup>[3]</sup> In addition to the prompt (by prompt we mean occurring on a sufficiently fast timescale that it was not possible to temporally resolve the emission from the  $\mu$ s UV pump pulse) blue luminescence feature at 435 nm (as distinct from the blue fluorescence observed in natural diamond at 425 nm), we have also observed a green luminescence signature centered at approximately 499 nm which decays on a much longer ms timescale. While this 499 nm luminescence signature has been observed before in synthetic CVD diamonds, it has never been reported in natural diamond.<sup>[4–7]</sup> This suggests that it has the potential to be used as an additional means of detecting specific synthetic diamonds which exhibit blue luminescence. We

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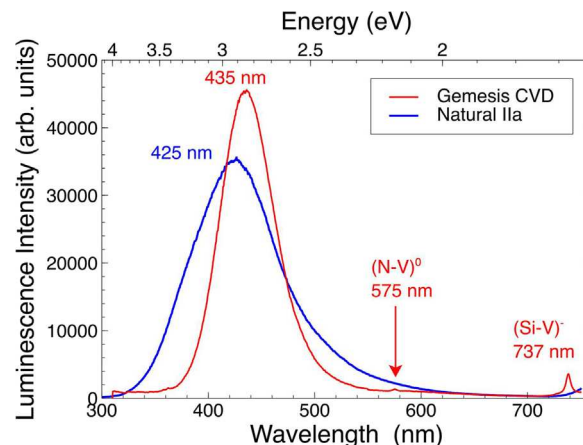
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further explore the spectroscopic properties of this green 499 nm feature in this paper. By comparing our data against a series of well-documented synthetic CVD diamond samples which have been annealed at a range of different temperatures, we speculate that a  $\text{Si}_x\text{N}_y$  complex or possibly a  $\text{Si}_x\text{N}_y$  vacancy ( $\text{Si}_x\text{N}_y\text{-V}$ ) complex is the origin of the underlying defect responsible for the 499 nm luminescence feature (where  $x$  and  $y$  are small value integers describing the stoichiometry of the complex).

## 2. Luminescence Data for Synthetic Diamond Gemstones

The starting point for our investigations was a set of three commercially sourced CVD synthetic diamond gemstones from Gemesis. The stones were graded by the International Gemological Institute and their findings are summarised in Table 1. While we have no information on the growth parameters, some interesting clues may be found in a spectroscopic study performed by Wang et al. on CVD diamond material from Gemesis.<sup>[8]</sup> Particularly relevant is the authors' conclusion that there is a strong likelihood that the CVD samples have undergone post-growth HPHT processing to enhance their color and possibly their clarity. The gemstones first caught our attention after we recorded a blue fluorescence signature during UV illumination. This prompted us to perform a more detailed photoluminescence study. For the optical pump, we employed a spectrally filtered xenon flash lamp with UV emission confined to 190–227 nm by a bespoke band-pass filter from Laser Components. The temporal width of the UV pulse was measured to be 2.9  $\mu\text{s}$  at full width half maximum. The full details of the equipment used to perform the experiments are described later in Section 6. A prompt photoluminescence signal centered at 435 nm contemporaneous with the UV pump pulse was detected and is shown in Figure 1. The recorded photoluminescence signal shows some well-known features such as the neutral nitrogen vacancy center ( $\text{N-V}^0$ ) at 575 nm and the charged silicon vacancy center ( $\text{Si-V}^-$ ) at 737 nm, in addition to the blue broadband luminescence centered at 435 nm. We also imaged the spatial pattern of the prompt luminescence during UV illumination in the three CVD gemstones using a high-efficiency low-noise CMOS camera with global shutter, as shown in Figure 2. This approach differs from DiamondView in that the camera and UV source are synchronised on a  $\mu\text{s}$  timescale as described in the experimental section. We noted that the spatial pattern/distribution of the luminescence has distinct similarities to the blue fluorescence pattern typically observed for type IIa diamonds. A fluorescence image for a type IIa natural gemstone, recorded under similar conditions, is shown in Figure 3 for comparison. In these natural gemstones, the origin of this blue fluorescence is thought to be dislocations within the diamond



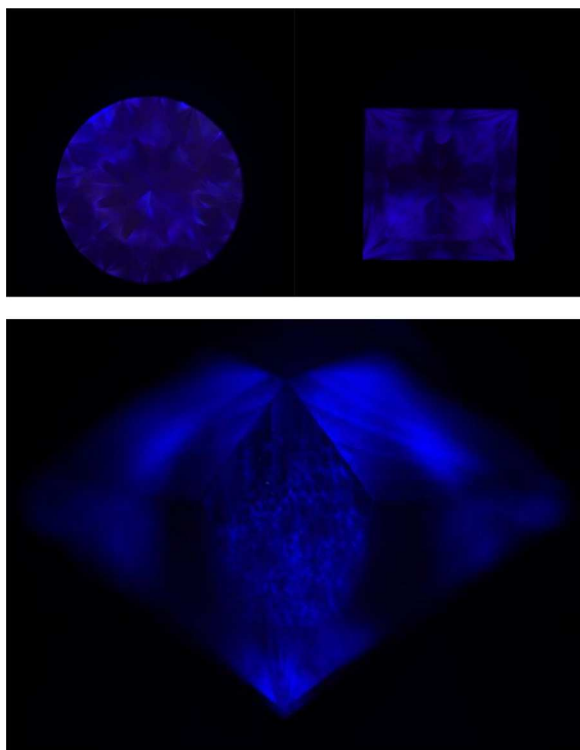
**Figure 1.** Comparing prompt blue luminescence spectra under UV illumination. The luminescence from the synthetic Gemesis diamond gemstone (sample 3) and the natural type IIa diamond are centred 435 nm at 425 nm, respectively. The Gemesis diamond shows a small additional emission peak at 737 nm attributed to the charged silicon vacancy center ( $\text{Si-V}^-$ ), indicating the presence of silicon in the diamond.

lattice.<sup>[9]</sup> The characteristic blue luminescence patterns in the fluorescence image of a diamond gemstone which demark dislocation networks in type II diamonds, or growth zone in type I diamonds, have often been used as supporting evidence for the gemstone's natural origin, but our observations indicate that this feature alone should not be used to determine a diamond's natural origin. During our spectroscopic study, we noticed an additional delayed luminescence signal not normally observed in natural diamond. After the prompt blue luminescence centered at 435 nm decayed, a much weaker long-lived green luminescence signal centered at 540 nm dominated the spectrum, as shown in Figure 4, with a sharp spectral feature centered at 499 nm. The spatial pattern/distribution of this long-lived green luminescence was recorded in the CMOS image shown in Figure 5. We performed a time-resolved measurement of the luminescence signal at 499 nm and the results are presented in Figure 6. The luminescent decay typically lasts several ms after the initial UV pump pulse, and the peak could still be detected after 1 s. We observed the same behavior in all three samples, but the strongest signal was found in sample 3. Such timescales are usually associated with phosphorescent decays. Very little information about this spectral line can be found in the current literature. The first report of a spectral line matching this wavelength is in a paper by Khong and Collins.<sup>[4]</sup> They observed a feature centered at 2.48 eV (approximately 499 nm) in the cathodoluminescence spectrum of three synthetic diamond samples. Two of these samples were grown in different institutes by a microwave assisted CVD technique, and the third sample

**Table 1.** International Gemological Institute grading results for the three synthetic CVD gemstones sourced from Gemesis.

Sample	Description	Shape & cutting Style	Measurements	Carat weight	Color grade	Clarity grade	Cut grade
1	Laboratory grown diamond	Round brilliant	4.40 × 2.70 mm	0.33	F	VVS2	Excellent
2	Laboratory grown diamond	Square modified brilliant	3.6 × 3.59 × 2.45 mm	0.28	E	SI2	–
3	Laboratory grown diamond	Square modified brilliant	4.09 × 4.05 × 2.81 mm	0.41	F	VVS1	–



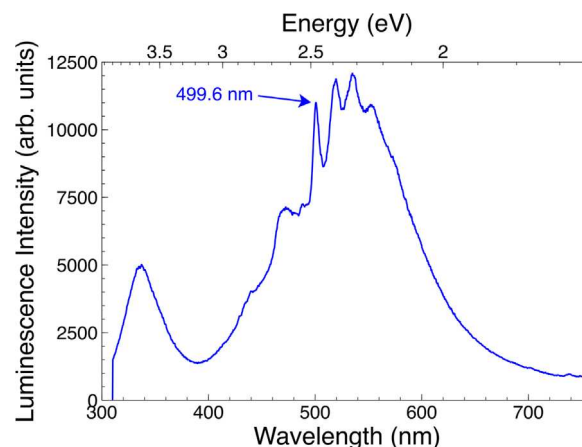


**Figure 2.** CMOS images of the prompt blue luminescence signal, recorded for the three Gemesis synthetic CVD diamond gemstones. Top: Samples 1 and 2, imaged from the top of the stone, looking directly down on the table. Bottom: Sample 3 (which had the strongest 499 nm emission), imaged from the side showing the crown and the pavilion.

was grown by a combustion flame technique. The authors do not report whether any post processing treatments were performed after growth. All three samples showed four cathodoluminescence peaks at 2.33, 2.42, 2.48, and 2.57 eV. The peaks in the two microwave assisted CVD samples appear significantly broader than in the sample produced by flame combustion. While the relative intensities of the peaks changed significantly between each sample, a correlation was found between integrated intensities of the 2.42 eV feature and the 2.57 eV feature. Since

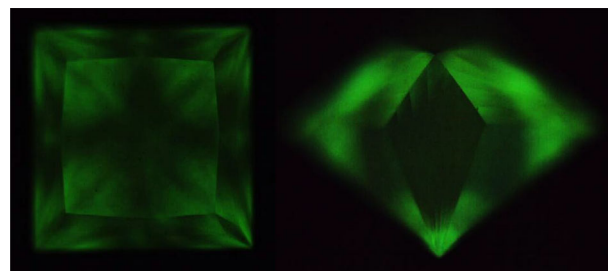


**Figure 3.** CMOS image showing the spatial distribution of the prompt blue luminescence signal exhibited by a typical type IIa natural diamond.

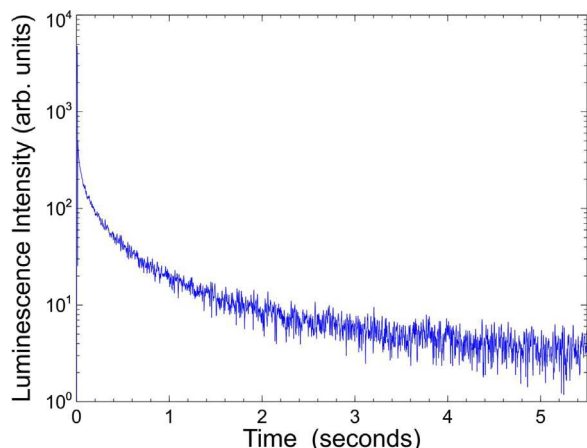


**Figure 4.** Delayed luminescence signal recorded after the initial prompt luminescence had decayed for the synthetic Gemesis diamond gemstone (sample 3). This spectrum was recorded after a delay of 100  $\mu$ s after the rising edge of the UV pump pulse and integrated for 60 ms.

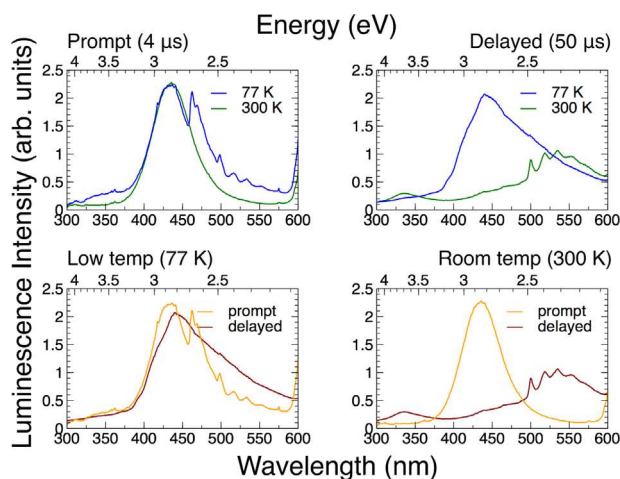
the energy spacing between these peaks was about 158 meV, the authors speculate that the 2.42 eV peak is a phonon replica of the 2.57 eV peak. There is a weak inference in this paper that the origin of the 2.48 eV (499 nm) spectral line is due to a defect incorporated during growth. There is further mention of a spectral line matching this wavelength in a second paper by the same authors,<sup>[5]</sup> and a paper by Kawarada et al., published the following year.<sup>[6]</sup> In the Kawarada paper, the diamond samples were also grown by microwave assisted CVD, and the 2.48 eV (499 nm) feature was observed in the cathodoluminescence spectrum. The only other reference to a spectral line matching this wavelength that we are aware of is in a short communication by Kitawaki et al. from the Central Gem Laboratory, Tokyo, concerning measurements made on undisclosed CVD diamond samples.<sup>[7]</sup> The authors simply report that under 325 nm excitation, 462 and 499 nm peaks with unknown origins were detected, although no spectra were included in this communication to aid comparison. They also speculate that the samples may have undergone post-growth HPHT treatment. We have found no reports of a spectral line at 499 nm in any literature pertaining to natural diamond. This seems to support Khong and Collins' original speculation that this line originates from an



**Figure 5.** CMOS images of the delayed 499 nm luminescence signal, recorded for the Gemesis synthetic CVD diamond gemstone (sample 3). The image was recorded at room temperature with a delay of 100  $\mu$ s after the rising edge of the UV pump pulse and integrated for 60 ms.



**Figure 6.** Semi logarithmic plot of the intensity of the 499 nm luminescent signal from sample 3 as a function of time. The luminescence signal lasts more than 1 s. The decay cannot be fitted to a simple mono-exponential or double-exponential function. As we have no a priori information relating to the luminescence decay mechanism, we parameterised the decay with a four-exponential function and extracted an average decay time of 1.06 s.

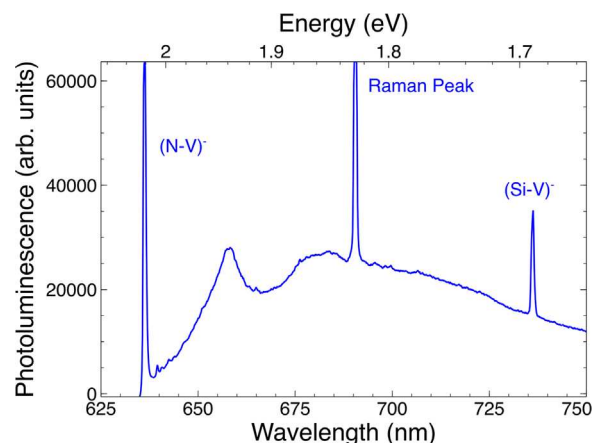


**Figure 7.** Comparing the luminescence characteristics at room temperature and 77 K on two different timescales. The prompt spectrum was recorded with recorded with zero delay from the rising edge of the UV pump of the UV pump, and integrated for 10  $\mu$ s. A delay of 100  $\mu$ s was used before recording the weaker long-lived luminescence, and the signal was integrated for 60 ms. Top left: Highlighting the difference between the prompt fluorescent signal at room temperature and 77 K. In addition to other substructure, there is a peak at 499 nm in the low temperature spectrum. Top right: The luminescence is markedly different on the different timescales. At 77 K the luminescence is broad with peak emission at blue wavelengths while the peak wavelength shifts to longer green wavelengths at room temperature and the 499 nm peak is now present. Bottom left: Highlighting the difference between the luminescence at 77 K for the two timescales. The prompt fluorescent signal has more substructure and shows a peak at 499 nm. Bottom right: At room temperature the prompt emission is predominantly blue, centered on 435 nm, but shifts to longer green wavelengths on the longer ms timescales.

impurity incorporated during growth, although we note that no information was reported about post growth heat treatment in this paper. In addition to room temperature measurements, we further investigated the behavior of this spectral line at low temperature (77 K). The three synthetic CVD gemstones exhibited similar luminescence behavior, although the signal was strongest is sample 3. **Figure 7** shows both the prompt (contemporaneous with the UV pump pulse) and delayed luminescence spectra (recorded at a delay of 100  $\mu$ s with respect to the rising edge of the UV pump) at room temperature and at 77 K. This figure highlights that upon cooling to 77 K, the decay life-time markedly decreases, so that the spectral feature was instead observed in the prompt luminescence spectrum. There was no evidence of any sub structure at green wavelengths for long (ms) timescales when the sample temperature is 77 K. We were not, however, able to rule out that luminescent emission at 499 nm also occurs on similar fast timescales at room temperature because the prompt blue luminescence may have swamped this weaker signal.

### 3. Luminescence Comparison with Annealed CVD Diamonds

Proceeding under the assumption that this 499 nm line originates from an impurity incorporated during growth, we searched through our library of synthetic CVD diamonds for evidence that this spectral feature had been previously observed in our material. We found a match in a series of well-documented CVD samples with high nitrogen concentration that were unintentionally doped with silicon and subsequently annealed at high temperatures. The material originated from Element Six (E6) and nitrogen had been intentionally introduced into the plasma at a level of 1.85 ppm during growth. The sample was grown on a polycrystalline substrate that was subsequently removed by laser cutting and polishing. The evidence for silicon



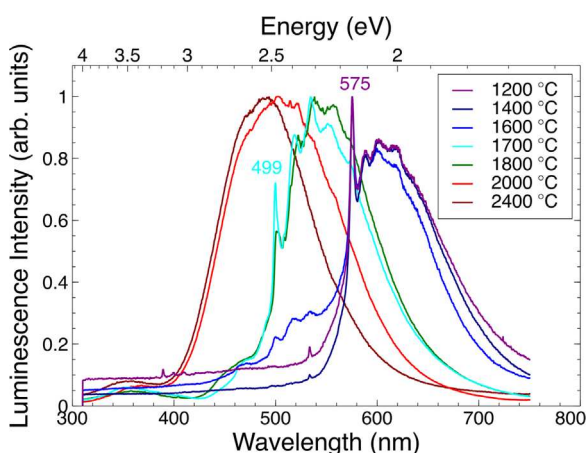
**Figure 8.** Photoluminescence spectrum for a pump wavelength of 633 nm recorded at 77 K. The spectrum shows a sharp peak at 737 nm, which is attributed to the charged silicon vacancy center (Si-V)<sup>-</sup>, and provides compelling evidence that the E6 CVD diamond contains a significant concentration of silicon.

**Table 2.** Annealing conditions, along with physical dimensions and carat weight, for each of the samples cut from the original E6 CVD nitrogen-doped diamond plate with high silicon concentration and independently heat treated.

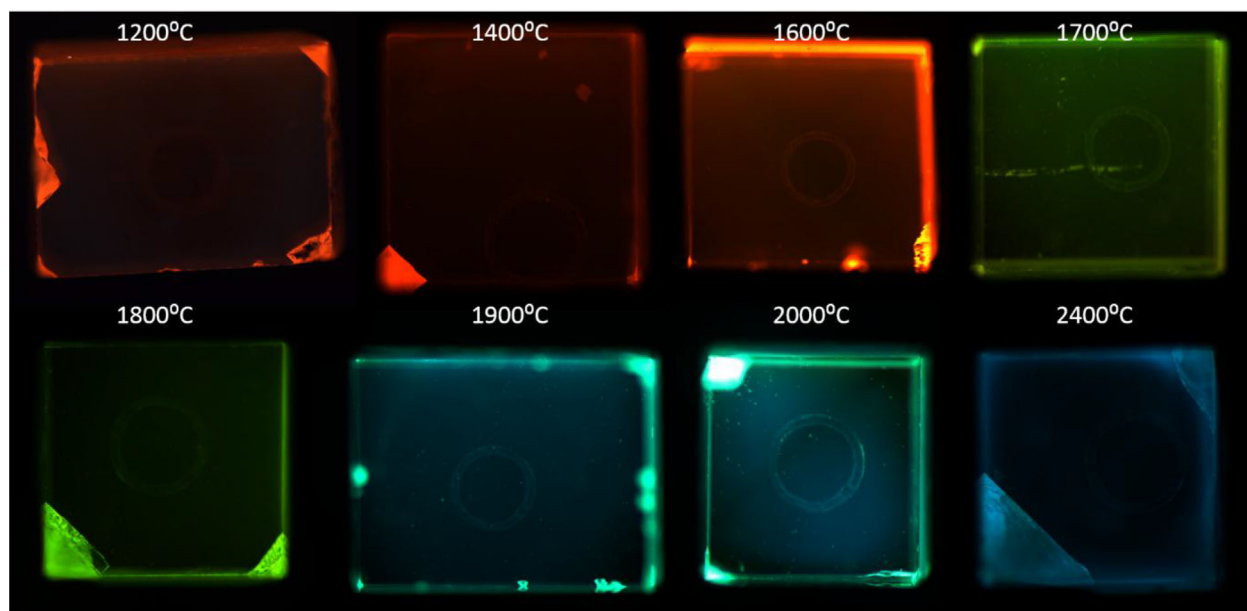
Sample	Shape & cutting style	Annealing conditions	x (mm)	y (mm)	z (mm)	Carat weight
A	Free standing film	1200 °C/4 h	5.05	3.73	1.45	0.47
B	Free standing film	1400 °C/4 h	3.56	3.58	2.228	0.49
C	Free standing film	1600 °C/4 h	4.73	4.16	2.176	0.75
D	Free standing film	1700 °C/4 h	4.00	4.21	2.22	0.65
E	Free standing film	1800 °C/4 h	3.59	3.48	1.71	0.36
F	Free standing film	1900 °C/4 h	5.21	3.99	2.146	0.77
H	Free standing film	2000 °C/4 h	3.29	3.44	1.964	0.38
I	Free standing film	2400 °C/4 h	3.29	3.35	2.018	0.36

incorporation in the CVD diamond came from the 633 nm photoluminescence spectrum recorded 77 K. This photoluminescence spectrum, shown in **Figure 8**, exhibited the characteristic sharp peak at 737 nm attributed to the (Si-V)<sup>-</sup> defect center. Silicon is an interesting impurity, because it is associated with CVD growth and only very rarely found in natural diamond.<sup>[9]</sup> The silicon is thought to originate from the quartz windows typically found on the CVD plasma chamber, and it is incorporated into the diamond crystal lattice during growth. Spectral evidence of a complex involving silicon would thus provide strong evidence that the diamonds were of synthetic CVD origin. The E6 CVD sample was cut into 8 similar sized pieces and each piece was annealed at a different temperature. The details are summarized in **Table 2**, which records the anneal conditions along with the physical dimensions and carat weight of each sample. **Figures 9 and 10** highlight how the wavelength

of the long-lived luminescence changes across the annealing sequence. **Figure 9** shows the luminescence spectra recorded at a delay of 100 μs after the rising edge of the UV pump pulse and **Figure 10** shows the spatial distribution of the luminescence recorded using a low-noise CMOS camera. For the lower annealing temperatures (1200–1400 °C), the long-lived luminescence appears red, mainly due to the presence of (N-V)<sup>0</sup>. This reddish color begins to fade as the nitrogen vacancies become mobile at higher annealing temperatures and aggregate with other defects. Consequently, the sharp (N-V)<sup>0</sup> peak at 575 nm disappears from the luminescence spectrum. Above 1600 °C, the emission is predominantly green due to the formation of the 499 nm feature and its associated vibronic side bands. At the highest annealing temperatures above 2000 °C, the emission appears turquoise, when the complex responsible for the 499 nm peak dissociates. The turquoise color is thought to be associated with N-B donor-acceptor pairs. The spectroscopic features associated with the changes in emission color were investigated further. There was no evidence of a 499 nm spectral line in the sample material before annealing. However, a small subset of the anneal temperatures showed the presence of this spectral line in the delayed luminescence spectrum. The 499 nm line was only observed in samples that had been annealed above 1600 °C and below 2000 °C. The strongest peak intensity was found in the sample which had been annealed at 1800 °C. This suggests a defect becoming mobile or breaking down above 1600 °C is involved in the formation of the defect responsible for the 499 nm emission. Since nitrogen vacancies are known to become mobile at this temperature,<sup>[10–12]</sup> and since silicon incorporation is associated with CVD growth, this led us to speculate that a complex involving both silicon and nitrogen is responsible for the 499 nm emission. To investigate the involvement of silicon in the 499 nm defect, we performed a further set of measurements on a second set of samples which had similar nitrogen concentration but where additional care had been taken to ensure that no silicon was introduced during growth. We treated this reference sample similarly, cutting it into a series of smaller pieces and annealing the samples under similar conditions. **Table 3** records the sample details and the corresponding annealing temperature. **Figure 11** shows the CMOS images recorded under similar UV illumination conditions. The low-silicon samples exhibit similar luminescence behavior with a comparable progressive color change from



**Figure 9.** Room temperature delayed luminescence spectra for the series of annealed E6 CVD diamond samples with high silicon and nitrogen concentrations annealed at different temperatures. This figure demonstrates that the 499 nm spectral line was only observed for samples which were annealed at temperatures in the range 1600–2000 °C. Note also that the sharp line at 575 nm, which is attributed to the (N-V)<sup>0</sup> defect, is not observed in the delayed luminescence spectrum for samples annealed at temperatures higher than 1600 °C, which provides further supporting evidence for our hypothesis that mobile nitrogen vacancies at elevated temperatures are involved in the formation of the 499 nm defect.



**Figure 10.** Composite CMOS image recording the luminescence from the 8 high concentration silicon-doped samples under UV illumination. This figure highlights a progressive color change from red through green and then turquoise with increasing annealing temperature.

red through green and then turquoise with increasing annealing temperature. However, this time spectroscopic measurements revealed no evidence of the 499 nm spectral line for any of the annealed samples, on any timescale. **Figure 12** shows the luminescence spectrum for the sample 3 which has been annealed at 1800 °C. There is no evidence of any spectral line at 499 nm. The nearest sharp observable spectral feature is located at 503 nm, which is known to be due to the H3 defect, a neutral complex containing two nitrogen atoms and a vacancy,  $(N-V-N)^0$ .<sup>[13]</sup> We have not observed H3 in the samples containing both nitrogen and silicon. We speculate therefore that the 499 nm forms preferentially over H3. Importantly, this result also indicates that nitrogen alone is not sufficient to make this defect. Combining the information from all these results, leads us to conclude that the origin of the 499 nm spectral line in the luminescence spectrum is a  $Si_xN_y$  (or possibly a  $Si_xN_y-V$ ) complex. Since the spectral line is also not present in silicon-nitrogen containing samples which have been annealed above 2000 °C we can also infer that the color center dissociates above this temperature. Unfortunately, we were not able to correlate this result with the expected reduction in silicon vacancies because the concentration of silicon in the samples was too low to observe changes in the  $(Si-V)^-$  peak at 737 nm.

#### 4. Discussion

The detection of a luminescence line at 499 nm, here attributed to a  $Si_xN_y$  or  $Si_xN_y-V$  color center provides a possible additional means of the detecting synthetic diamonds. High concentrations of silicon in diamond are normally associated with CVD growth. It is generally accepted that silicon can be unintentionally introduced to the CVD process by plasma-related etching of the quartz walls or windows of the reactor chamber, or from the

substrate during heteroepitaxial growth on silicon. An important signature of silicon incorporation is the silicon vacancy center  $(Si-V)^-$  line at 737 nm.<sup>[9]</sup> Diamond may also be intentionally doped with silicon by introducing silane into the plasma, and careful studies have revealed many other silicon-related spectral lines.<sup>[9,12]</sup> Natural growth conditions do not favor the incorporation of larger atoms such as silicon into the compact diamond lattice.<sup>[14]</sup> However, the presence of silicon alone is not sufficient to rule out that the diamond is not of natural origin. A very small number of natural diamonds containing the  $(Si-V)^-$  center have been previously reported by Breeding and Wang.<sup>[9]</sup> In their report, FTIR analysis revealed that the diamonds included both type IIa diamonds and type Ia diamonds with nitrogen concentrations ranging from 0 to 4.7 ppm, predominantly in the form of A-aggregates. However, Breeding and Wang did not report a 499 nm line in their comprehensive spectral study of these natural samples. To our knowledge, the 499 nm line has only ever been observed in synthetic diamond and thus we believe it has the potential to be used to detect such synthetic diamonds. Since the 499 nm line has only been observed in samples that have been annealed in a narrow temperature window between 1600 and 2000 °C, it could also be used to detect whether a diamond has been heat treated in this temperature range. In their recent investigation of synthetic CVD diamond sourced from Gemesis, Wang et al. have stated that spectroscopic evidence indicates a likelihood that the CVD synthetics have undergone post-growth HPHT processing to enhance their color and possibly their clarity.<sup>[8]</sup> Long-lived color centers in diamond are also interesting for other reasons and might be exploited in other technology applications.  $(Si-V)^-$  centers are already generating considerable excitement as single photon sources.<sup>[15–17]</sup> The 499 nm center might find application as a buffer for the temporary storage of quantum information in a diamond quantum technologies platform based on silicon impurities.



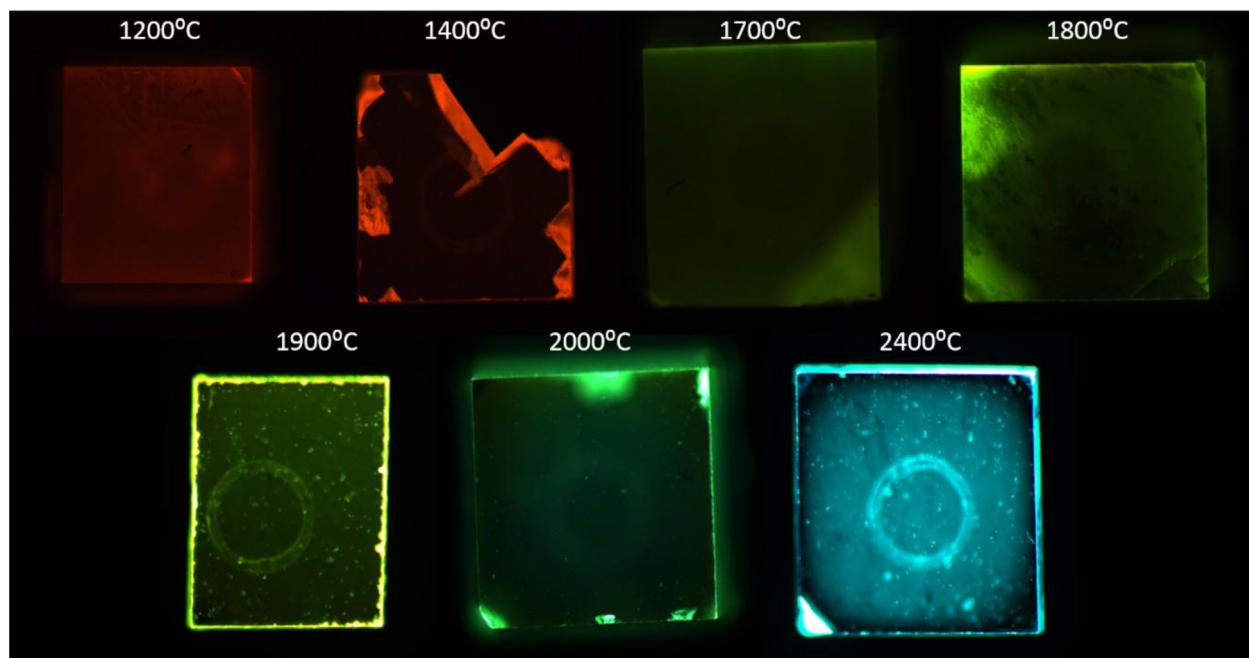
**Table 3.** Annealing conditions, along with physical dimensions and carat weight, for each of the samples cut from the original E6 CVD nitrogen-doped diamond plate with low silicon concentration and independently heat treated.

Sample	Shape & cutting style	Annealing conditions	x (mm)	y (mm)	z (mm)	Carat Weight
A	Free standing film	1200 °C/4 h	3.32	3.07	2.956	0.57
B	Free standing film	1400 °C/4 h	3.18	3.15	0.53	0.07
D	Free standing film	1700 °C/4 h	3.38	3.15	3.45	0.64
E	Free standing film	1800 °C/4 h	3.32	3.01	2.696	0.46
F	Free standing film	1900 °C/4 h	3.22	2.67	0.50	0.07
H	Free standing film	2000 °C/4 h	3.25	2.97	3.386	0.53
I	Free standing film	2400 °C/4 h	3.45	3.37	0.52	0.10

## 5. Conclusion

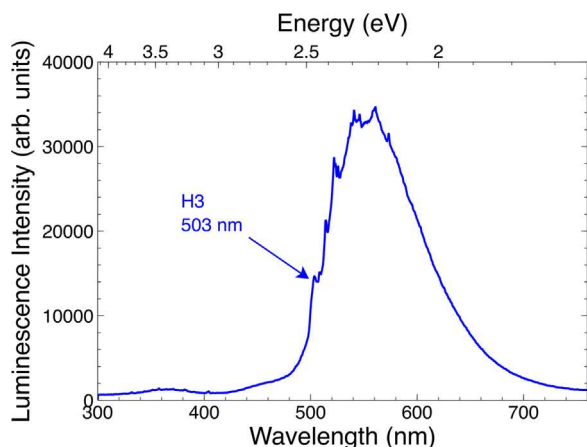
We have investigated the properties of a sharp spectral feature centered at 499 nm in CVD synthetic diamond gemstones. These gemstones also exhibited the blue luminescence normally indicative of type IIa natural diamonds, although on close inspection, the spectral characteristics were subtly different. The luminescence peak was centered at 435 nm in the synthetic CVD gemstones as compared to 425 nm in type IIa gemstones. While a spectral line matching the 499 nm wavelength has been previously observed in CVD diamond, this is the first time it has been seen in synthetic gemstone-quality material. The luminescence lifetime is very long, typically lasting longer than 1 s after the UV excitation pulse. We also found the same spectral feature in a set of well-documented CVD diamond with high concentrations of both nitrogen and silicon which had undergone different annealing

treatments. The 499 nm line was only observed in samples which had been annealed in the temperature range 1600–2000 °C at which temperature nitrogen vacancy centers are known to become mobile, indicating the involvement of nitrogen in the defect's structure. Heat treatment at temperatures above 2000 °C removed the color center. We also performed a comparison with similar CVD material known to have comparable nitrogen concentration but negligible silicon content which had undergone similar heat treatment. The absence of the 499 nm spectral line in the samples that were not unintentionally silicon doped leads us to conclude that both silicon and nitrogen are necessary for the formation of this color center. Our results suggest that the presence of this spectral line could be used as an additional means of detecting specific synthetic diamonds which might otherwise be mistaken for a type IIa natural diamond.



**Figure 11.** Composite CMOS image recording the luminescence in from the 7 samples with negligible silicon under UV illumination. This figure highlights a similar progressive color change (from red through green and then turquoise) with increasing annealing temperature to the silicon-doped samples shown in the previous figure.





**Figure 12.** Delayed luminescence spectrum of CVD diamond material with high nitrogen content and negligible silicon concentration which has been annealed at 1800 °C. The arrow pointing toward 503 nm shows the H3 defect (N–V–N)<sup>0</sup>.

## 6. Experimental Section

The light source used was a Hamamatsu Photonics L7685 xenon flash lamp spectrally filtered to 190–227 nm output, with temporal pulse width of 2.9 μs at full width half maximum. The UV emission was confined to 190–227 nm by a bespoke band-pass filter from Laser Components. In the context of this work, “prompt luminescence” was recorded contemporaneously with the lamp pulse, while delayed luminescence was recorded after the initial prompt luminescence signal decayed.

Spectral data was recorded using the Horiba iHR-320 spectrometer with 300 g mm<sup>−1</sup> grating and the flash lamp synchronised with an Andor iStar DH320T-18U-E3 Intensified CCD (iCCD). A pulse generator was used to provide two TTL signals to the xenon flash lamp and to the iCCD. The iCCD signal is delayed by 8 μs with respect to the flash lamp to account for the difference in latency between the two devices. To record prompt luminescence, the iCCD delay was set to zero, with emission integrated over a 10 μs gate. To record delayed luminescence, the iCCD delay was set to 100 μs with emission integrated over a 60 ms gate. In both measurements, 40 accumulations were averaged.

The imaging was carried out with the same filtered xenon flash lamp as used for the spectra and recorded using a Basler Ace acA1920-40 μm area scan camera, synchronised in the same way as the Andor iStar.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

diamond, luminescence, nitrogen, silicon, vacancy

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